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(11) Publication No.: **0 057 884 B2**

(12)

NEW EUROPEAN PATENT

(45) Publication Date of the New Patent:
April 15, 1992, Patent Bulletin 92/16

(51) Int Cl.⁵: **C07C 209/00, C07C 211/13,
C07C 215/00, C07C 217/04,
C07C 211/4**

(21) Application number: **82100669.9**

(22) Date of filing: **January 30, 1982**

(54) **Method for the Production of Permethylated Oligoamines and Aminoalkanols**

The file contains technical information that was submitted after receipt of the application and is not contained in this patent.

(30) Priority: **February 11, 1981, Germany, 3104738**

(43) Publication Date:
August 18, 1982, Patent Bulletin 86/14

(45) Announcement of Patent Granting:
April 2, 1986, Patent Bulletin 86/14

(45) Announcement of Decision Concerning Opposition:
April 15, 1992, Patent Bulletin 92/16

(84) Designated Contracting States:
BE DE FR NL

(56) Literature Cited:

**EP-A-0 006 454
DE-A-2 709 864
DE-A-2 824 908
DE-A-2 838 184
DE-A-3 116 395
DE-B-2 535 073
FR-A-2 065 046
US-A-2 412 209**

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Description

The invention relates to a method for the production of permethylated oligoamines and aminoalkanols (especially N,N,N',N'-tetramethyldiaminoalkanes and oxaalkanes) by means of the reaction of the corresponding diols or amino alcohols, via the intermediate stage of the corresponding N,N-dimethylaminoalkanols, with dimethylamine in the gas phase on a fixed bed catalyst, preferably at atmospheric pressure.

The production of tertiary aliphatic monoamines by means of the reaction of aliphatic alcohols or aldehydes with primary or secondary amines in the presence of cobalt and/or copper catalysts in the liquid phase is known from DE-A-535 073.

The production of amino alcohols by means of the reaction of glycols with ammonia in the presence of hydrogenation catalysts (for example, Raney nickel, copper chromite, copper/nickel chromite, iron, cobalt, titanium or copper) is described in US-A-2 412 209.

EP-A-6454 teaches the production of peralkylated polybasic amines by means of the reaction of a diol with a secondary amine in the liquid phase at a hydrogen pressure of more than 5 bar and in the presence of a catalyst containing copper and chromium as essential active components.

It is also known that monoalcohols and the corresponding carbonyl compounds or ketones can be made to react with dimethylamine. Methods of this type are described in DE-A-2 709 864 and DE-A-2 838 184. On the other hand, to date there have obviously been insurmountable difficulties in applying this interesting reaction to diols and N,N-dimethylaminoalkanols, since other paths have thus far been pursued to produce N,N,N',N'-tetramethyldiaminoalkanes and oxaalkanes. The reaction of bis-(2-chloroethyl) ether with dimethylamine and the reaction of N,N-dimethyl-1-amino-2-chloroethane with sodium N,N-dimethylaminoethanolate are described in DE-B-1 795 762. An attempt has also been made to reach the goal by means of the reaction of diamines with formaldehyde and subsequent hydrogenation.

These methods have a number of shortcomings. Either toxicologically harmful substances are used or the end product contains too much incompletely methylated diamine. Significant expenses and a number of process steps are therefore required in these methods to arrive at a pure end product.

It was found that permethylated oligoamines and aminoalkanols are obtained in good yield, if the corresponding N,N-dimethylaminoalkanols or diols or their mixtures are converted

in the gas phase with dimethylamine on copper-rich catalysts containing aluminum oxide. Both pure alkanediols and diols in the broader sense, i.e. compounds whose carbon framework is interrupted by heteroatoms, are suitable as diols. Ethanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol and 1,10-decanediol; on the one hand, and diethylene glycol or N-methyl-diethanolamine, on the other, are suitable.

One allows the reaction to run preferably at atmospheric pressure or slightly above it at a reaction temperature between 100 and 200°C, expediently using a tubular reactor with a fixed bed catalyst. A carrier gas for the reaction partner is essential, since the reaction temperature generally lies below the boiling point of the diols; hydrogen is particularly well suited.

An amount of carrier gas between 10 and 1000 times the reaction space, which is continuously circulated, is generally required. Space velocities (h^{-1}) from 50 to 1000 times the reaction space can be set. The amount of diol or dimethylaminoalkanol contained in the gas stream naturally depends on its vapor pressure under the reaction conditions. Conversion rates (space-time yields) from 0.02 to 0.5 volume parts diol (liquid) or dimethylaminoalkanol per volume part of reaction space are normally achieved. The amount of dimethylamine to be maintained in the gas stream is obtained from the stoichiometry. A certain excess of dimethylamine is preferably used so that 1 to 3, especially 1 to 1.5 mol dimethylamine is present per mol equivalent of OH groups. The dimethylamine leaves the reactor and the connected condensation system in three different ways:

- 1) by chemical reaction
- 2) in dissolved form in the reaction product
- 3) as a gas in the circulating gas.

The dimethylamine taking path 1 is replaced by fresh dimethylamine. The dimethylamine proceeding along path 2 is recovered during known workup of the reaction product and fed back to the reactor.

The copper fraction in the copper-rich aluminum oxide catalyst should expediently be more than 20 wt%.

The reaction temperature lies in the range between 100 and 200°C. The reaction is slow and incomplete in the lower range and almost stops completely under 100°C. In the upper range byproducts are increasingly formed so that the production of the desired products gradually

becomes uneconomical because of increasing losses and mounting difficulties in the separation of the byproducts.

For practical execution of the method, the reactants are best fed to an evaporator together with the hydrogen serving as carrier gas and then to the reactor.

A tubular reactor is preferred because the reaction temperature can be adjusted most precisely in this case. The catalyst is generally arranged within the tube, while the space between the tubes is traversed by a heat transfer medium. The catalyst can be present in the form of cylindrical pellets and also in the form of extrudates with a diameter of a few mm or in other form.

Since the copper is initially present in the fresh catalyst in oxide form, it must be converted to the metallic state by activation. This occurs in the known fashion with a hydrogen-nitrogen gas mixture, for example, at a temperature between 120 and 250°C.

The operating pressure is generally close to atmospheric pressure. It was observed that a higher pressure, for example even 3 bar gauge pressure, leads to an increased formation of byproducts. For example, the percentage of N,N,N'-trimethyldiaminoalkane in the reaction product increases from a few tenths of a percent to more than 1%.

The formation of N,N,N',N'-tetramethyldiaminoalkane is particularly preferred, if the corresponding N,N-dimethylaminoalkanol is used as reaction partner. In some cases this intermediate (partially converted product) can be favorably obtained by means of an independent reaction. N,N-dimethylaminoethanol can be easily obtained by means of the reaction of ethylene oxide with dimethylamine. In other cases, this type of compound is not readily available. However, it is formed as the intermediate product in each case during the reaction of the corresponding diols with dimethylamine and sometimes even forms the only byproduct.

By adjusting suitable reaction conditions, one can arrive at a situation in which N,N-dimethylaminoalkanol predominates as the reaction product. This is done, for example, by reducing the reaction temperature, by shortening the residence time, smaller supply of dimethylamine or a combination of these measures.

The N,N-dimethylaminoalkanol obtained as the main or byproduct can be obtained in high purity by means of distillation at reduced pressure. There are also application possibilities for this product, for example, in the production of certain dyestuffs. Generally, the partially converted products are mixed with an appropriate amount of the corresponding diol and sent

back to the reactor via the evaporator. A high yield (generally above 70%) of N,N,N',N'-tetramethyldiaminoalkane is obtained in this way.

Example 1

Preparation of N,N,N',N'-tetramethyl-1,6-diaminohexane from hexanediol and dimethylamine

A cylindrical tube 40 mm in diameter and 2500 mm long served as reactor. The volume filled with catalyst was 3000 cm³. The tube was enclosed by a jacket traversed by a heat transfer agent. The evaporator was situated above the reactor. It was also designed like the reactor, but had a length of only 700 mm and was packed with Raschig rings made of metal. Its jacket space was traversed by the same heat transfer agent as that of the reactor.

A water cooler, a first separator, a brine cooler and a second separator were situated beneath the reactor. The fractions of the reaction product condensable at -10°C were taken off here as liquid, while the carrier gas was fed back to the evaporator by means of a gas circulation pump. Dimethylamine and hexanediol were added to the circulating gas at the evaporator input and completely evaporated. Since hexanediol has a melting point above 40°C, it was used as a 75% methanolic solution in the interest of simplicity.

200 cm³ per hour was evaporated from this solution. The circulating gas contained about 20 vol% dimethylamine. Overall the amount of circulating gas was 400 NL/h.

The copper-aluminum oxide catalyst described in DE-PS 2 445 303 served as the catalyst in the form of cylindrical pellets 4 mm in diameter, which had been reduced at 140 to 200°C with a mixture of 10 vol% hydrogen and 90 vol% nitrogen.

The reaction runs at 160°C. The condensates formed in the separators were combined, analyzed by gas chromatography and fractionated: ignoring methanol, dimethylamine and the formed water, the condensate consisted of 90% N,N,N',N'-tetramethyl-1,6-diaminohexane, 2% N,N,N'-trimethyl-1,6-diaminohexane and 8% other byproducts. Fractional distillation yielded a high-purity product.

Example 2**Preparation of N,N,N',N'-tetramethyl-1,5-diamino-3-oxapentane**

150 cm³/h of a mixture consisting of the same molar fractions of diethylene glycol and N,N-dimethylamino-3-oxapentan-5-ol was fed to the installation and catalyst of example 1.

The circulating gas contained 20 vol% dimethylamine. The entire amount of circulating gas was 600 NL/h.

The reaction was run on the catalyst at 145°C.

The collected condensates were analyzed by gas chromatography and worked up by fractional distillation. Ignoring dimethylamine and water, the condensate consisted of 30 wt% N,N,N',N'-tetramethyl-1,5-diamino-3-oxapentane, 63 wt% N,N-dimethylamino-3-oxapentan-5-ol and 7 wt% byproducts.

Fractional distillation yielded a high-purity product.

Example 3**Preparation of N,N,N',N'-tetramethyldiaminoethane**

The procedure described in example 1 was followed.

150 cm³/h N,N-dimethylaminoethanol was supplied to the evaporator. The circulating gas contained 8 vol% dimethylamine. The entire amount of circulating gas was 600 NL/h.

The reaction was run on the catalyst at 150°C. The condensates collected in the separators were analyzed again and fractionated.

Ignoring dimethylamine and reaction water, the condensate consisted of 36 wt% N,N,N',N'-tetramethyldiaminoethane, 58 wt% N,N-dimethylaminoethanol and 6 wt% byproducts.

Fractional distillation and drying yielded a high-purity product.

Claims

1. A process for the preparation of permethylated oligoamines and aminoalkanois by the reaction of a diol, an ether diol, an N,N-dimethylaminoalkanol or an azaalkanol with dimethylamine, with or without the intermediate stage of the N,N-dimethylaminoalkanol, under conditions of hydrogenation/amination, wherein the reaction is carried out in the gas phase under essentially atmospheric pressure, at from 100 to 200°C, over a copper-rich catalyst containing an aluminum oxide.
2. A process as claimed in claim 1, wherein hydrogen is circulated as the carrier gas, and the reaction products are obtained from the circulating gas stream by cooling.